L. J. BRATZLER, MILDRED E. SPOONER, J. B. WEATHERSPOON
and JEANNETTE A. MAXEY
Department of Food Science, Michigan State University
East Lansing, Michigan 48823

Smoke Flavor as Related to Phenol, Carbonyl and Acid Content of Bologna

SUMMARY—Phenol, carbonyl and acid determinations were made on layers of bologna that had been smoked during processing. Similar samples were evaluated for intensity of smoke flavor by taste panel. Correlation coefficients between phenols, carbonyls, acids and taste panel evaluation of smoke flavor intensity were 0.81, 0.37 and 0.32, respectively. Thus, phenols appear to be the principal contributor to smoke flavor and aroma.

INTRODUCTION

THE PRACTICE of smoking foods is an old process. It is thought to have developed as an adjunct to the drying method of preserving meat and fish by hanging the product over a fire or in a room in which a fire was maintained for warmth or cooking purposes. In addition to the preservation by dehydration, the bactericidal and antioxidant properties of the smoke also increased the storage stability of the treated meat or fish. Since controlled refrigeration is used to protect many foods from rapid deterioration and spoilage, meat products are generally smoked for the distinctive surface color development and the characteristic smoke flavor.

The components of smoke responsible for the distinctive flavor are found in the steam-distillable fraction and are mainly phenols, acids and carbonyls (Husaini et al., 1957). Tilgner et al. (1962b) reported that the main components of the steam-distillable fraction of wood-smoke condensate were carbonyls, 24.6%, acids (carboxylic), 39.9%, and phenols, 15.7%. Tucker (1942) and Kurko (1959) found that phenols were present in decreasing amounts from the outer to inner portions of smoked ham or sausage. Acid penetration of 10 to 12 mm into fresh ham was reported by Hamid et al. (1966).

The present study was undertaken to determine the relation of phenols, carbonyls and acids to smoke flavor as determined by taste panel.

METHODS AND MATERIALS

A BOLOGNA emulsion was stuffed into No. 5 Tee-Pak Clear Zip Fibrous casings (Tee-Pak, Inc.). The ingredients were as follows:

Pork trimmings	9.2 lb	Sodium nitrate	1.4 g
Beef trimmings	9.2 lb	Sodium nitrite	1.4 g
Nonfat dried milk	0.9 lb	Sodium ascorbate	4.0 g
Ice	5.9 lb	Sugar	32.6 g
		Salt (NaCl)	152.0 g

No spices were used because of the possible interference with taste panel evaluation. The bologna was processed in an air-conditioned smokehouse that had about 5 air changes per minute. Smoke was generated from smoldering, dampened hardwood sawdust. A temperature of 140°F and a relative humidity of 23% was maintained for the first 2 hr of processing. The temperature was then raised to 160°F with a relative humidity of 31% until the bologna reached an internal temperature of 128°F. The smokehouse temperature was then maintained at 160°F by injecting high pressure steam only, which resulted in 69% relative humidity. Total smoking and processing time was about 4 hr. The bologna was showered with cold water until the internal temperature was reduced to 90°F and then stored in a 36°F cooler.

Consecutive outside-to-inside layers were removed from the sticks of bologna for chemical analyses and taste-panel evaluation. They were 1.4 to 1.6 mm thick and were identified by the letters A-H (outer to inner). Samples for chemical analyses were ground 5 times through a 1.5-mm plate. Consumer-type panels varying from 18 to 30 members were used. Panelists were served samples that were 2.5 × 5.0 cm × 1.6 mm in size and were asked to score the samples from 1 to 7, where 1 = no smoke flavor and 7 = very strong smoke flavor.

Carbonyl determination

Carbonyls were determined by the method of Batzer et al. (1957). The carbonyl-free benzene, carbonyl-free ethanol, saturated 2,4-dinitrophenylhydrazine solution, 4% trichloroacetic acid solution, and the 4% KOH solution were prepared as outlined by Henick et al. (1954).

A 1- to 2-g sample of ground bologna was blended with 40 ml of carbonyl-free benzene and 40 ml of carbonyl-free ethanol in a Waring blender for 2 min. The slurry was filtered through Whatman No. 1 filter paper into a 100-ml volumetric flask. Carbonyl-free benzene was used to rinse the blender and filter paper slurry and to bring the filtrate to volume. A 2-ml aliquot of well-mixed filtrate, 3 ml of saturated 2,4-dinitrophenylhydrazine, and 3 ml of 4% trichloroacetic acid were added to a 25-ml volumetric flask. It was stoppered and placed in a 60 ± 5°C water bath for 30 min and then cooled to room temperature.

Color development was obtained by addition of 5 ml freshly filtered 4% KOH, and the solution was brought to volume with carbonyl-free ethanol. Absorbance values were read at 430 mμ with a Beckman spectrophotometer exactly 10 min after adding the KOH solution. The 2,4-dinitrophenylhydrazone of n-heptaldehyde in appropriate concentrations was used for the standard curve.

Acid determination

Milliequivalents of acid were determined by the method suggested by Hamid et al. (1966). An accurately

weighed 1- to 2-g sample of ground bologna was blended with 50 ml of distilled water in a Waring blender for 2 min. The blender was thoroughly rinsed with distilled water and the resultant slurry titrated to pH 8.3 with 0.2 *N* NaOH.

Phenol determination

The method of Tucker (1942) was used to estimate total phenols, which are reported as phenol, although they could have been based on 2,6-dimethoxyphenol or guaiacol.

A 20-g sample of the ground bologna was placed in a Waring blender with 100 ml of 50% ethyl alcohol and mixed at full speed for 5 min. The extract was filtered through S and S (Schleicher & Schuell) No. 560 hand-folded filter paper. The filtrate container was covered and allowed to stand for 12 to 16 hr at 2 to 4°C. It was then filtered through Whatman No. 2 filter paper.

The diluted or undiluted samples (based upon yellow color development) as well as the standard solutions were transferred to 15 × 180 mm test tubes. The standards contained varying amounts of phenol from 0.0 mg to 0.5 mg per 100 ml. Five ml of a 5% solution of sodium borate ($Na_2B_4O_7.10\ H_2O$) were added to a 5-ml sample of the diluted or undiluted extracts and the standard tubes. Color was developed by the addition of 1 ml of a *N*, 2,6-trichloro-p-benzoquinoneimine solution. This stock solution contained 0.25 g in 30 ml of ethyl alcohol. Color was allowed to develop 1½ hr at room temperature.

The samples and standards were added to separatory funnels containing 15 ml of N-butanol. After the solutions were shaken and allowed to separate, the water layers were drawn off and discarded. The butanol layers were transferred to graduated test tubes and brought to 21 ml by adding N-butanol. Finally, 2 ml of N-butanol saturated with NH_3 were added and the contents thoroughly mixed. The solutions were read in a Bausch and Lomb Spectronic 20 colorimeter at 635 mμ.

RESULTS AND DISCUSSION

THERE WAS a gradual decrease in the amount of phenols present in the outer to the inner layers of the bologna (Table 1). Tucker (1942) reported 1.36 mg phenols per 100 g of "lean surface tissue" and 0.32 mg per 100 g of "lean tissue ½ in. below lean surface" for ham smoked 24 hr. Sample size was 50 g but no indication was given as to sample thickness. In the present study, since the bologna emulsion contained no phenols, and the amount in the inner layer was very small, it is reasonable to assume that phenols are a good indicator of the amount of smoke deposition and also of smoke penetration.

Table 1. Phenol, carbonyl and acid values,[1] and panel smoke perception scores [2] from the emulsion and 1.6 mm layers A-H of a typical bologna stick.

Layer	Phenols mg/100 g	Carbonyls mg/100 g	Acids meq/100 g	Panel smoke perception scores
A (outer)	3.70	1.38	4.47	....
B	2.04	1.17	5.48	5.8
C	1.41	1.23	5.51	5.1
D	1.02	1.06	6.58	4.4
E	0.78	1.09	7.01	3.9
F	0.43	1.22	6.86	3.5
G	0.26	1.24	6.37	3.1
H (inner)	0.12	1.05	8.72	2.9
Emulsion	0.00	1.21	5.35	....

[1] Fresh basis.
[2] 1 = no smoke flavor; 7 = very strong smoke flavor.

The amount of carbonyls in the bologna layers showed little difference from that in the emulsion before heating and smoking (Table 1). An increase was expected because carbonyls have been found to comprise 24.6% of the steam-distillable fraction of wood smoke (Tilgner et al., 1962b). In the present study the lack of a marked increase in carbonyl content due to smoking may have been due to the possible screening effect of the cellulose casing. However, Simon et al. (1966) found that water-filled cellulose casings were good absorbent systems for the phenols, acids and carbonyls in wood smoke.

The variability in the acid data (Table 1) may have been influenced to some extent by the processing (heating) of the meat component of the bologna. Hamid et al. (1966) found 0.05 meq of acid per gram for the lean of unsmoked fresh ham. They exposed pieces of the ham to known acid volatiles for 2 hr and obtained over 0.45 meq/g from the outer surface when isocaproic acid was used. Their results indicated a maximum acid penetration depth of 10 to 12 mm. A similar approximate penetration was observed in the present study based on the phenol data but the acid results were too variable to support the same conclusion.

Thirty-one samples of bologna were scored for smoke-flavor intensity and similar samples were analyzed for phenol, carbonyl and acid content. Different degrees of smoke flavor were obtained by presenting various layers to the panels. The outer, or A layer, was never used as it was dark in color and also dry in appearance. It was found that the panelists had difficulty in detecting differences in smoke-flavor intensity between adjacent layers. Therefore, the panelists were asked to score nonadjacent layers, with no more than 4 samples presented at a single session.

A correlation coefficient of 0.81 ($P < .01$) was determined when phenol content was compared with panel scores. This relationship agrees with the conclusions of researchers who studied the flavor characteristics of phenols as a group, or of phenolic components. Tilgner et al. (1962a) found that water solutions of smoke-phenolic fractions were characterized as "cured-smoky" by a sensory panel. They reported that threshold values ranged from 0.15 to 1.09 ppm of phenols expressed as resorcin.

Fiddler et al. (1966) stated that preliminary studies indicated the essential smoke odor was in the phenolic portion of their smoke condensate from hickory sawdust. Wasserman (1966) combined the three major phenolic components—guaiacol, 4-methylguaiacol, and 2-6 dimethoxyphenol—in the same proportion as they occurred in the smoke condensate analyzed by Fiddler et al. (1966), and observed the resulting mixture to have an odor only slightly similar to the smoke condensate.

Correlation coefficients of 0.37 ($P < .05$) and 0.32 were calculated when panel scores were compared with car-

bonyl and acid content, respectively. Carbonyl content accounted for about 14% of taste panel variation, whereas phenols accounted for 66% of panel variation. While the correlation (0.32) between panel scores and acid content approached statistical significance, it only accounted for 10% of the variation between panel scores and meq of acids present in the bologna.

Under the conditions of the present study, it can be concluded that phenols are a good indicator of smoke flavor intensity as evaluated by taste panel.

REFERENCES

Batzer, O. F., Sribney, M., Doty, D. M. and Schweigert, B. S. 1957. Production of carbonyl compounds during irradiation of meat and meat fats. *Agric. and Food Chem.* **5**, 700–703.

Fiddler, W., Doerr, R. C., Wasserman, A. E. and Salay, J. M. 1966. Composition of hickory sawdust smoke: furans and phenols. *Agric. and Food Chem.* **14**, 659–662.

Hamid, H. A. and Saffle, R. L. 1966. The penetration depth of volatile fatty acids into fresh ham. *Food Technol.* **20**, 224–225.

Henick, A. S., Benca, M. F. and Mitchell, J. H. Jr. 1954. Estimating carbonyl compounds in rancid fats and foods. *Jour. American Oil Chem. Soc.* **31**, 88–91.

Husaini, S. A. and Cooper, G. E. 1957. Fractionation of wood smoke and the comparison of chemical composition of sawdust and friction smokes. *Food Technol.* **11**, 499–502.

Kurko, V. 1959. A rapid determination of the smoke phenols penetrating sausages. Mayasn. Ind. SSSR 30, 17. From translation by E. Wierbicki.

Simon, S., Rypinski, A. A. and Tauber, F. W. 1966. Water-filled cellulose casings as model absorbents for wood smoke. *Food Technol.* **20**, 1494–1498.

Tilgner, D., Miler, K., Prominski, J. and Darnowska, G. 1962a. The sensoric quality of phenolic and acid fractions in curing smoke. In "Advances in the Engineering of the Smoke-Curing Process," ed. Tilgner, D., pp. 37–39. Yugoslav Institute of Meat Technology. Beograd, Yugoslavia.

Tilgner, D. J., Ziminska, H. and Wronska-Wojciechowska, M. 1962b. The chemical and sensorial characteristics of the steam volatile components in smoldering and friction smoke. In "Advances in the Engineering of the Smoke Curing Process," ed. Tilgner, D., pp. 35–36. Yugoslav Institute of Meat Technology. Beograd, Yugoslavia.

Tucker, I. W. 1942. Estimation of phenols in meat and fat. *J. Assoc. Offic. Agr. Chemists* **25**, 779–782.

Wasserman, A. E. 1966. Organoleptic evaluation of three phenols present in wood smoke. *J. Food Sci.* **31**, 1005–1010.

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